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METHOD FOR CLEANING FILTER MEMBRANE MODULE  
[Rokamaku mojjyuhru no senjyoh houhoh]

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## Claims

1. A method for cleaning a filter membrane module to restore water permeability by cleaning a filter membrane module degraded in water permeability of the membrane in a purifying system for water by means of a liquid chemical, which method for cleaning a filter membrane module is characterized by the fact that a pressurizing process for pressurizing with a gas is provided from the permeation side of the filter membrane of the filter membrane module at least at one point of time before or after the liquid chemical is supplied to the filter membrane module, or at both points of time, under a pressure of at least 20 kPa but below the bubble point for 0.1-5 min.

2. The method for cleaning a filter membrane module described in Claim 1, characterized by the fact that the water used is ground water.

3. The method for cleaning a filter membrane module described in Claim 1 or 2, characterized by the fact that the filter membrane is an ultrafiltration membrane.

4. The method for cleaning of a filter membrane module described in one of Claims 1-3, characterized by the fact that the filter membrane module is a hollow yarn membrane module comprising a hollow yarn membrane.

5. The method for cleaning of a filter membrane module described in one of Claims 1-4, characterized by the fact that the material used for the membrane of the filter membrane is cellulose acetate.

6. The method for cleaning of a filter membrane module described in one of Claims 1-5 characterized by the fact that cleaning with a liquid chemical is done with one type or two or more different types of chemicals selected from among citric acid, a surfactant and sodium hypochlorite in a single step or a multiple-step combination.

## Detailed explanation of the invention

[0001]

### Technical field of the invention

The present invention pertains to a method for cleaning filter membrane modules, and the invention further pertains to a method for cleaning filter membrane modules capable of restoring water permeability in a short cleaning time when cleaning the filter membrane module with a liquid chemical to restore water permeability and cleaning, making safe operation possible for a long time after cleaning.

[0002]

### Prior art and problems to be solved by the invention

In the past, as a method for cleaning a filter membrane module with reduced water permeability using a liquid chemical, for example, a method for cleaning a filter membrane module consisting of circulating a liquid chemical upon equalizing the pressure of the permeating liquid and the pressure of the stock solution is disclosed in Japanese Kokai Patent Application No. Sho 61[1986]-11108. Furthermore, a method for cleaning a filter membrane module consisting of injecting a liquid chemical from the permeation side is disclosed in Japanese Kokai Patent Application No. Hei 3[1991]-77629 and Japanese Kokai Patent Application No. Hei 4[1992]-161232, etc. The problem with the methods of the aforementioned cases is that a sufficient cleaning effect cannot be achieved when a cleaning method where a liquid chemical alone is used. When the cleaning effect achieved is insufficient, the amount of liquid chemical used is increased or the cleaning time with the chemical is increased in an attempt to improve the cleaning effect in the aforementioned prior art.

[0003]

Furthermore, a method for cleaning a filter membrane module consisting of injecting a gas from the permeation side is disclosed in, for example, the technical journal, "Membranes" Vol. 20, No. 5, p. 328 (1995). The method disclosed is a back washing method in which the gas injected from the permeation side instantaneously passes through the filter membrane and removes clogging substances to restore the filter flow velocity. However, the injection of gas in this case is not a cleaning method used at the time of a liquid chemical cleaning process, and as a consequence, removal of substances such as iron oxide and manganese oxide adsorbed on the filter membrane is not possible.

[0004]

Based on the above background, the purpose of the present invention is to provide a method for cleaning a filter membrane module capable of sufficiently removing materials adsorbed to the filter membrane, improving efficiency of cleaning, and at the same time, reducing the amount of the liquid chemical used, so that cleaning with a liquid chemical can be done in a short time, and furthermore, the cleaning cost can be decreased in a liquid chemical cleaning process for filter membranes.

[0005]

Means to solve the problem

As a result of much research conducted by the inventors of the present application on feeding of a liquid chemical to the filter membrane module and timing of application of pressure, etc., during the course of the cleaning process with a liquid chemical of a filter membrane module, they found a significant difference in the cleaning effect based on the timing of the pressure applied and the pressure of the gas used, and as a result of further study of types of filter membranes, a combination of the liquid

chemical and the order and number of cleanings with the liquid chemical, etc., the inventors discovered that a superior cleaning effect could be achieved in a short time, and as a result, the present invention was accomplished.

[0006]

Thus, the method for cleaning filter membrane module of the present invention is a method characterized by the fact that a pressurizing process using a gas is provided from the permeation side of the filter membrane of the filter membrane module at least at one point of time before or after the liquid chemical is supplied to the filter membrane module, or at both points of time, under a pressure of at least 20 kPa but below the bubble point for 0.1-5 min in a method for cleaning a filter membrane module for restoring water permeability by cleaning a filter membrane module with degraded water permeability in a membrane purifying system for water by means of a liquid chemical.

[0007]

Furthermore, the method for cleaning filter membrane module of the present invention is characterized by the fact that the water used is ground water.

[0008]

Furthermore, the method for cleaning a filter membrane module of the present invention is characterized by the fact that the filter membrane is an ultrafiltration membrane.

[0009]

Furthermore, the method for cleaning a filter membrane module of the present invention is characterized by the fact that the filter membrane module is a hollow yarn membrane module using a hollow yarn membrane.

[0010]

Furthermore, the method for cleaning a filter membrane module of the present invention is characterized by the fact that the material used for the membrane of the filter is a cellulose acetate.

[0011]

And furthermore, the method for cleaning filter membrane module of the present invention is characterized by the fact that the cleaning with a liquid chemical is done with one or two or more different types of chemicals selected from citric acid, a surfactant and sodium hypochlorite in a single step or in a multiple steps.

[0012]

Embodiment of the invention

In the present invention, pressurizing with a gas may be provided at least at one point of time before or after the liquid chemical is supplied to the filter membrane module, or at both points of time, and it is desirable when provided either before or before and after the liquid chemical is supplied. In order to physically remove the substances adsorbed on the surface of the filter membrane and to further enhance the cleaning efficiency with the liquid chemical, it is desirable when the aforementioned treatment is done prior to supplying the liquid chemical to the filter membrane module. In the method for cleaning a

filter membrane module of the present invention, the pressure used for introducing of the gas from the permeation side of the filter membrane module is at least 20 kPa but below the bubble point, and at least 40 kPa but below 150 kPa is further desirable. In this case, the reason the pressure of the gas used is specified to be at least a pressure of 20 kPa but below the bubble point is because the cleaning effect is insufficient when the gas pressure used is less than 20 kPa, and the target cleaning recovery cannot be achieved; on the other hand, when the pressure used is at the bubble point or above, the filter membrane module may be physically damaged. In this case, the bubble point varies depending on the material used for the filter membrane, the fraction molecular weight of the filter membrane and the pore diameter of the membrane, and for example, in the case of an acetate cellulose film having a membrane pore diameter of 0.1  $\mu\text{m}$ , a gas pressure of approximately 300 kPa is used.

[0013]

Furthermore, it is not necessary for the gas to permeate the filter membrane and reach the stock solution side at the time of introducing the gas to the permeation side of the membrane in the gas compression process as long as the gas is injected inside the film in the thickness direction from the permeation side of the filter membrane. When injection of the gas is carried out as explained above, the gas enters inside the entire filter membrane in the thickness direction of the filter membrane and the substances clogging the filter membrane are pressed out and uniform cleaning of the interior of the filter membrane module is made possible. When a liquid (liquid chemical) is applied from the permeation side of the filter membrane module as in the case of standard backwashing process, the liquid permeates through regions of the membrane with a lower degree of clogging and permeation through the clogged area is less likely to occur, thus, [complete] cleaning of the clogged regions cannot be achieved and cleaning of the filter membrane becomes non-uniform.



[0014]

In this case, the compression time of the gas (gas compression process) is the duration of time that the gas is applied to the permeation side of the entire filter membrane of the filter membrane module and in general, 0.1-5 min is desirable, and when the cleaning effect and cleaning efficiency are taken into account, 0.5-2 min is desirable. In this case, the reason the compression time of the gas is specified to be in the range of 0.5-5 [sic] min is because the gas cannot sufficiently reach the clogged areas and cleaning efficiency for the clogged area is insufficient when the compression time is .5 min or less; on the other hand, when the compression time is 5 min or longer, an increase in the additional cleaning effect cannot be expected and the cleaning efficiency is reduced.

[0015]

The filter membrane used for the filter membrane module of the present invention is not especially limited, and for example, a microfiltration membrane, ultrafiltration membrane, nanofiltration membrane, reverse osmosis membrane, etc., can be mentioned. When a gas is applied from the permeation side in the microfiltration membrane, permeation of the gas through the filter membrane occurs at times, and as a consequence, uniform cleaning cannot be achieved. Furthermore, in the case of a nanofiltration membrane or reverse osmosis membrane, the pore diameter of the filter membrane is too small and infiltration of the gas into the pores of the filter membrane is insufficient at times; and as a result, uniform cleaning cannot be achieved. For the reasons given above, an ultrafiltration membrane is desirable for the filter membrane of the present invention. In this case, ultrafiltration membrane means a filter membrane having a fraction molecular weight in the range of  $10^3$ - $10^6$  and a pore diameter in the range of 1-100 nm.

[0016]

As for the film material used for the filter membrane module of the present invention, polymer materials such as polyether sulfone, polyacrylonitrile copolymer and cellulose acetate can be mentioned, and among those listed above, cellulose acetate is especially desirable.

[0017]

As for the form of the membrane of the filter membrane module of the present invention, the plate and frame type, pleated type, spiral type, tubular type (pipe-like type), or hollow yarn type can be mentioned, and among those listed above, the hollow yarn type is especially desirable. Furthermore, when a hollow yarn membrane module is used, the internal pressure system in which the stock solution flows inside the hollow yarn membrane is desirable.

[0018]

As an example of the present invention where cleaning with a liquid chemical is performed with one or two or more different types of chemicals, use of a "combined liquid chemical" consisting of citric acid and a surfactant can be mentioned. Furthermore, the aforementioned single step or a combination of multiple steps with the aforementioned liquid chemical means cleaning once with the aforementioned liquid chemical in a single step or cleaning multiple times with the liquid chemical in multiple steps. As an example of cleaning the filter membrane module using citric acid and a surfactant, many different combinations, for example, (1) an example where cleaning is first performed with citric acid followed by cleaning with a surfactant, (2) cleaning multiple times with a liquid chemical containing both, etc., can be mentioned. Needless to say, the gas pressurizing process may be applied before, during or after

the aforementioned cleanings. The liquid chemical used at the time of the liquid chemical cleaning may be circulated in the untreated water side of the filter membrane or may be circulated from the untreated water side to the permeation side. Furthermore, the liquid chemical may be circulated from the permeation side of the filter membrane to the untreated water side as well.

[0019]

#### Working examples

The present invention is further explained in detail with working examples and the figures appended below, but the present invention is not limited by these working examples. Figure 1 is a schematic view of a membrane purifying system 10, which is a membrane cleaning system utilized in cleaning filter membrane modules 11A-E in the filter membrane module cleaning system of the present invention, and accessories such as flow meter and pressure gage are omitted in the figure. In Figure 1, 11 is a filter membrane module and consists of a combination of five modules and each is defined as filter membrane module 11A, 11B, 11C, 11D and 11E (represented by 11). In the filter membrane module 11, the material of the membrane used for the filter membrane 11R is a cellulose acetate, and represents a hollow yarn membrane module comprising a hollow yarn, and each hollow yarn membrane comprises a hollow yarn having an inner diameter of 0.8 mm and an outer diameter of 1.3 mm, and the membrane area of a single module is 0.5 m<sup>2</sup>. Furthermore, 12 is a pre-filter, and the pre-filter is used for removal of impurities included in the ground water, which is the water supplied to the filter membrane module 11. Furthermore, 13 is a permeated water tank, and the permeated water tank is used for temporary storage of the permeated water from the filter membrane module 11. Furthermore, 14 and 15 are pumps, and 6, 7 and 8 are two-way valves.

[0020]

In this case, two-way valve 7 is closed and two-way valves 6 and 8 are opened at the time of filtration treatment. The raw river water 1 used as the ground water is supplied from the water supply pipe 16, impurities are removed by the pre-filter 12 and the aforementioned ground water is supplied to five filter membrane modules 11A-11E by pump 14. In the filter membrane module 11, the raw river water is supplied to the hollow core of the hollow yarn membrane 11R, and the permeated water filtered by internal pressure cross flow filtration passes through the two-way valve 6 and is collected, temporarily stored in the permeated water tank 13 and is delivered from the pipe 17 as a purified water. The unfiltered untreated water passes through the two-way valve 8 through the circulating pipe 18 and is recycled. The filter of the filter membrane module 11 is a steady flow filtration at a set filtration flow velocity of 1.5 m/day at a cross flow line speed of 0.2 m/s. Furthermore, a back washing process consisting of supplying the permeated water from the permeation side of the filter membrane module for 1 min at a ratio of once every 45 min is provided and the water recovery percentage is 90%. During the course of the back wash operation, the two-way valve 7 is opened and the two-way valves 6 and 8 are closed and pump 14 is stopped. Furthermore, a back wash operation consisting of supplying a portion of the permeated water to the permeation side of the filter membrane module 11 through pump 15, which is the reverse of the normal operation, is periodically provided.

[0021]

#### Working Example 1

Figure 2 illustrates Working Example 1 of the present invention, and 20 is a membrane purifying system for filter membrane module used in the method for cleaning filter membrane module of the present invention. First, the structure of the membrane purification system 20 shown in Figure 2 is

explained. In this case, 21 is a filter membrane module, 22 is a liquid chemical tank for storing the liquid chemical 22A used for cleaning the filter membrane module, 23 is a pure water tank containing purified water, 24 is a pump, 25 is an pneumatic tank containing compressed air 25A used as a gas, 26 is a pressure gage, 27 is a pressure regulating valve, 28, 29, 30, 31, 32, 33, 34, 35, 36, 38, 39 and 40 are two-way valves and 37 is a filter. In the aforementioned membrane purification system 20, the valve of the pneumatic tank 25 is opened while the two-way valves 32 and 39 are closed and the pressure regulating valve 27 is adjusted so that the compressed air 25A can be injected into the permeation side of the filter membrane module 21 at a specific pressure. Furthermore, when pump 24 is turned on while two-way valves 29, 30, 33, 34, 35 and 40 are open and two-way valves 28, 31, 32, 36, 38 and 39 are closed, it is possible to circulate the liquid chemical 22A inside the liquid chemical tank 22 and to clean the filter membrane module 21 with the liquid chemical. After the cleaning is completed, the two-way valve 28 is opened to release liquid chemical 22A, then, two-way valves 31, 29, 33, 34, 36, 32 and 40 are opened and two-way valves 30, 28, 35, 38 and 39 are closed and the pump is turned on and the purified water permeation flow is measured to obtain the recovery ratio.

[0022]

In the aforementioned working example, first, five filter membrane modules 11A-E having a purified water permeation capacity with a purified water permeation flow rate of 8.4 m/day were mounted in the filter membrane module 11 in the membrane purification system 10 shown in Figure 1. Furthermore, untreated river water (ground water) 1 obtained from a river was supplied from water supply pipe 16, and filtration treatment was initiated. The filtration treatment in this case is an internal pressure cross flow filtration (cross flow line speed 0.2 m/s) in which the untreated water is supplied to the interior of the hollow yarn membrane and a steady flow filtration at a set filtration flow rate of 1.5 m/day was used.

In this case, a back wash process consisting of flowing the permeated water from the permeation side of the filter membrane module for 1 min was provided every 45 min during the operation to achieve a water recovery percentage of 90%. In the aforementioned filtration treatment under the steady flow filtration treatment, the filter membrane was contaminated with impurities included in the untreated water and the filter pressure slowly increased as a result of clogging, and the filter pressure reached 10 kPa in all of five filter membrane modules approximately 8 months after the start of the treatment and continued treatment was not possible. When the aforementioned five filter membrane modules 11A-11E were removed from the membrane purification system 10 and were replaced with the filter membrane module 21 of the membrane purification system 20 shown in Figure 2, and when purified water was filtered through the filter membrane module 11 under an air pressure of 100 kPa and the purified water permeation flow rate was measured, a value of 1.3-1.8 m/day was achieved in all cases and a significant reduction in the permeation performance from that of the initial purified water permeation flow rate of 8.4 m/day was observed.

[0023]

After the aforementioned treatment, cleaning was of the filter membrane module 11 was conducted. First, the filter membrane module 21 of the membrane purification system 20 was replaced with the filter membrane module 11A used for the aforementioned treatment (purified water permeation flow rate of 1.5 m/day), the air 25A with the air pressure adjusted to 50 kPa by the pressure regulating valve 27 was injected into the permeation side of the filter membrane module 21 from the pneumatic tank 25 for 1 min while the two-way valves 32 and 39 were closed. That is, a gas compression process was provided. Furthermore, in order to perform the liquid chemical cleaning, two-way valves 29, 30, 33, 34, 35 and 40 were opened and two-way valves 28, 31, 32, 36, 38 and 39 were closed, and pump 24 was turned on,

and furthermore, an aqueous solution of citric acid (1 wt%) inside the liquid chemical tank was circulated for 30 min under the mean line speed on the membrane surface of 0.5 m/s and cleaning was performed for the aforementioned filter membrane module with a liquid chemical; then, the two-way valve 28 was opened and the aforementioned liquid chemical was released. Subsequently, when the purified water permeation flow rate of the filter membrane module 11A was measured according to the procedure described above, a flow rate of 8.3 m/day was achieved, and an excellent cleaning efficiency, that is, an excellent recovery factor that was essentially the same as the permeation flow rate before the treatment was achieved.

[0024]

#### Working Example 2

In Working Example 2, the membrane purification system 10 described in Working Example 1 was used and the filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with the filter membrane module 11B (purified water permeation flow rate of 1.8 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. Furthermore, before injecting air to the permeation side of the filter membrane module 11B, an aqueous solution of citric acid (1 wt%) was circulated for 10 min to clean the membrane; then, compressed air 25A at an air pressure of 100 kPa was injected into the permeation side to bring the permeation side of the filter membrane module 11B so that it came in contact with air 25A for 1 min and at the same time, the liquid chemical 22A was released (that is, gas compression process). Furthermore, the aqueous solution of citric acid (1 wt%) was circulated for 10 min to clean the filter membrane module 11B and the liquid chemical was released for a second time. In other words, cleaning was performed with one type of liquid chemical in two steps, one before and one after the gas compression process. When the purified water

permeation flow rate of the filter membrane module 11B was measured, a rate of 8.0 m/day was obtained, and an excellent cleaning efficiency, that is, excellent restoration of the permeation flow rate to 95% of the value prior to treatment was achieved in a relatively short cleaning time of approximately 20 min with a liquid chemical.

[0025]

### Working Example 3

In Working Example 3, the membrane purification system 10 described in Working Example 1 was used, and the filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with filter membrane module 11C (purified water permeation flow rate 1.6 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. Furthermore, compressed air 25A with an air pressure of 50 kPa was injected from the permeation side of the filter membrane module 11C while the two-way valve 32 was opened and 39 was closed and brought into contact with the permeation side of the filter membrane module 11R for one minute (that is, gas compression process); then, the pump 24 was turned on while the two-way valves 28, 29, 30, 33, 34, 38 and 39 were opened and the two-way valves 27, 31, 32, 35, 36 and 40 were closed, and furthermore, a 1 wt% aqueous solution of a surfactant (Ultrasil #53, [transliteration] Product of Henchel Hakusui Co.) included in the liquid chemical tank 22 was injected from the permeation side of the filter membrane module 11C under a pressure of 100 kPa for 1 min. And finally, the liquid chemical was released. Furthermore, when measurements were made for the purified water permeation flow rate of the filter membrane module 11C, a rate of 7.6 m/day was obtained, and excellent cleaning efficiency, that is, restoration of the permeation flow rate to 90% of the value prior to [water] treatment was achieved in this case as well.



[0026]

#### Comparative Example 1

In Comparative Example 1, the membrane purification system 10 described in Working Example 1 was used and the filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with the filter membrane module 11D (purified water permeation flow rate 1.3 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. In this case, injection of compressed air to the permeation side of the filter membrane module 11D was omitted and an aqueous solution of citric acid (1 wt%) was circulated for 30 min as in the case of Working Example 1 and cleaning the filter membrane module 11D was performed, and the liquid chemical was subsequently released. Subsequently, when the purified water permeation flow rate of the filter membrane module 11D was measured, a rate of 5.6 m/day was achieved and the cleaning recovery factor measured was significantly lower and was only 65% of the permeation flow rate before [water] treatment even though approximately 30 min of the cleaning time was provided.

[0027]

#### Comparative Example 2

The filter membrane module 21 of the membrane purification system 20 shown in Figure 2 was replaced with the filter membrane module 11E (purified water permeation flow rate of the filter membrane module 11D, 1.6 m/day) with a reduced permeation performance as a result of steady flow filtration treatment. In this case, injection of compressed air to the permeation side of the filter membrane module 11E was omitted and a 1 wt% aqueous solution of a surfactant (Ultrasil #53, [transliteration] Product of Henchel Hokusui Co.) was injected from the permeation side of the filter

membrane module 11E under a pressure of 100 kPa according to the procedure described in Working Example 3 and cleaning was performed. Subsequently, the liquid chemical was released. When measurements were made, a rate of 4.3 m/day was achieved and the cleaning recovery factor was significantly lower at 51% of the permeation flow rate before [water] treatment.

[0028]

#### Effect of the invention

As explained in detail above, according to the present invention, a significant improvement in the cleaning efficiency of the filter membrane module can be achieved when a gas compression process is appropriately provided during a liquid chemical cleaning process, furthermore, a reduction in the amount of liquid chemical required is made possible, and furthermore, cleaning with a liquid chemical in a short time is possible, resulting in a significant reduction in the cleaning cost.

#### Brief description of the figures

Figure 1 is a schematic view of a membrane purification system utilizing a filter membrane module used in application of the method for cleaning a filter membrane module of the present invention.

Figure 2 is a schematic view of a liquid chemical cleaning device for filter membrane modules used for applying the method for cleaning filter membrane modules of the present invention.

#### Explanation of symbols

- 1      Untreated river water, surface water (water)
- 10     Membrane purification system (membrane cleaning system)
- 11     Filter membrane module (hollow yarn membrane module)

11R Filter membrane (hollow yarn membrane)

22A Liquid chemical

25A Air (gas)

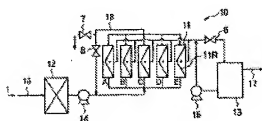


Figure 1

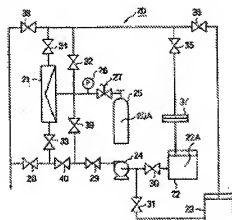


Figure 2